

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Appln. No: 10/591,632  
Applicant: Martyn Vincent Twigg  
Filed: September 5, 2006  
Title: METHOD OF MANUFACTURING A CATALYSED CERAMIC WALL-FLOW FILTER  
T.C./A.U.: 1793  
Examiner: Yoshitoshi Takeuchi  
Confirmation No.: 3293  
Docket No.: JMYT-370US

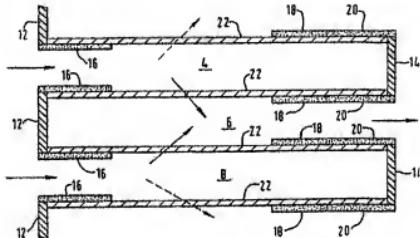
Commissioner for Patents  
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**DECLARATION OF PAUL J. ANDERSEN UNDER 37 C.F.R. 51.132**

I, Paul J. Andersen, being duly warned that willful false statements and the like are punishable by fine or imprisonment or both, under 18 U.S.C. §1001, and may jeopardize the validity of the patent application or any patent issuing thereon, state and declare as follows:

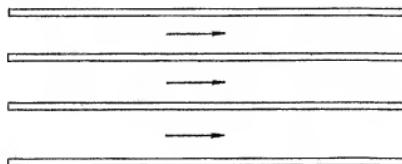
1. All statements herein made of my knowledge are true and statements made on information and belief are believed to be true.
2. I earned a B.S. in Chemical Engineering from the University of Illinois in Urbana, Illinois and a Ph.D. in Chemical Engineering from Northwestern University In Evanston, Illinois.
3. Since 1992, I have worked for Johnson Matthey PLC in the field of emission control catalysis. I am the Technical Director for the Stationary Emission Control business. I am responsible for the discovery of emission control catalyst materials, including materials suitable for use in three-way catalysts and oxidation catalysts, and the development of products incorporating such catalysts.

4. I am familiar with the differences between "wall-flow" filters and "flow-through" substrates, which are known generally in the industry.
5. A wall-flow filter has a plurality of channels plugged at an inlet end or an outlet end, which causes the gas to pass through the channel walls to reach the downstream end of the filter. An example of a wall-flow filter is depicted in Figure 1 of U.S. Patent No. 6,753,294:



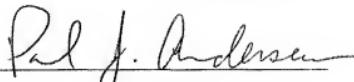
Thus, as is evident in the Figure, the plurality of channels 4, 6, 8 are plugged at an inlet end 12 or an outlet end 14. Therefore, any gas entering at channels 4, 8 must cross the channel walls to exit the filter.

6. A flow-through substrate, on the other hand, has a plurality of channels extending from one end to the other, which allows the gas to pass straight through the filter member. In other words, the gas is not forced to pass through or across channel walls. For example, a flow-through substrate may be depicted as follows:



7. For more information, an article from the Ceramic Industry entitled "Beyond Traditional Ceramic Honeycombs" is also attached for your consideration.

discussing the differences between flow-through substrates and wall-flow filters.



Paul J. Andersen

Paul J. Andersen

Date:

July 2, 2010

Enclosures: U.S. Patent No. 6,753,294  
Ceramic Industry Article



US006753294B1

(12) United States Patent  
Brisley et al.(10) Patent No.: US 6,753,294 B1  
(45) Date of Patent: Jun. 22, 2004

## (54) CATALYTIC WALL-FLOW FILTER

5,750,084 A \* 5/1998 Tsutsumi et al. .... 423/230.1

5,758,494 A 6/1998 Rao et al.

(75) Inventors: Robert James Briley, Cambridge (GB); Martyn Vincent Twigg, Cambridge (GB); Anthony John Joseph Wilkins, Essex (GB)

## FOREIGN PATENT DOCUMENTS

(73) Assignee: Johnson Matthey Public Limited Company, London (GB)

EP	0 056 584	7/1982
EP	0 277 012	1/1988
EP	0 341 832	11/1989
EP	0 736 713	2/1997
EP	0 814 242	12/1997
EP	0 834 343	4/1998
WO	99/39809	8/1999
WO	99/47260	9/1999
WO	00/29726	5/2000
WO	00/74823	12/2000

( \*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 223 days.

(21) Appl. No.: 09/807,571

## OTHER PUBLICATIONS

(22) PCT Filed: Aug. 14, 2000

International Search Report dated Dec. 19, 2000.

(86) PCT No.: PCT/GB00/03064

British Search Report dated Jan. 7, 2000.

§ 371 (c)(1),  
(2), (4) Date: Jul. 23, 2001

\* cited by examiner

(87) PCT Pub. No.: WO01/12320  
PCT Pub. Date: Feb. 22, 2001Primary Examiner—Stanley S. Silverman  
Assistant Examiner—Edward M. Johnson  
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## (30) Foreign Application Priority Data

Aug. 13, 1999 (GB) .....	9919013
(51) Int. Cl. ....	B01J 20/02
(52) U.S. Cl. ....	502/439; 502/400
(58) Field of Search .....	502/439, 302, 502/311, 350, 355, 340, 344, 339, 65, 305, 527.19

## ABSTRACT

A wall-flow filter for an exhaust system of a combustion engine comprises: a plurality of channels in honeycomb arrangement, wherein at least some of the channels are plugged at an upstream end and at least some of the channels not plugged at the upstream end are plugged at a downstream end; an oxidation catalyst on a substantially gas impermeable zone at an upstream end of the channels plugged at the downstream end; and a gas permeable filter zone downstream of the oxidation catalyst for trapping soot, in that in an exhaust system, preferably a diesel exhaust system, the oxidation catalyst, which preferably includes a platinum group metal, is capable of generating sufficient NO<sub>x</sub> from NO to combust the trapped soot continuously at a temperature less than 400° C.

## (56) References Cited

24 Claims, 1 Drawing Sheet

## U.S. PATENT DOCUMENTS

4,515,758 A	5/1985 Domesle et al.
4,857,089 A	8/1989 Kitaagawa et al.
4,902,487 A *	2/1990 Cooper et al. .... 423/215.5
5,089,237 A	2/1992 Schuster et al.
5,492,679 A	2/1996 Amend et al.
5,519,993 A	5/1996 Rao et al.

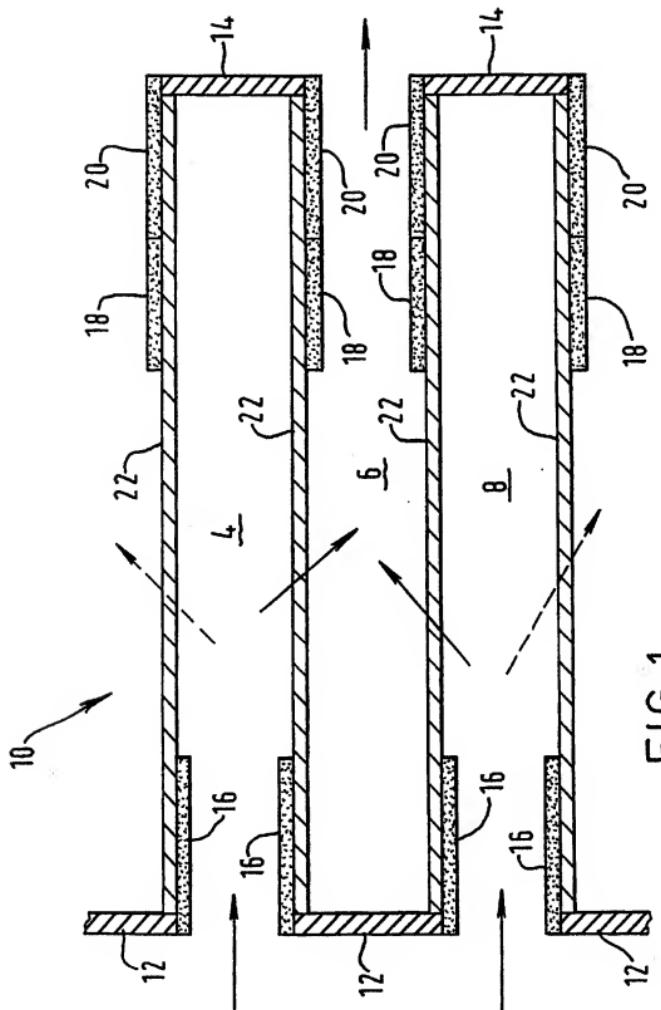


FIG. 1.

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CATALYTIC WALL-FLOW FILTER

This invention relates to a wall-flow filter, and in particular to a wall-flow filter including a catalyst.

Exhaust gases of a combustion engine contain a number of components linked with damaging health and the environment. One of these is the soot component. A way of controlling the amount of soot in the exhaust gas is to use a filter downstream from the exhaust manifold, the idea being to burn (oxidise) soot trapped on the filter, thereby regenerating the filter.

A known type of soot filter is the wall-flow filter. This filter can be made, for example, from a ceramic monolith including channels in a honeycomb arrangement. A typical embodiment has each channel plugged at one or other end thereof, and at the opposite end to the laterally and vertically adjacent channels. When viewed from either end, the alternately plugged and open ends of the channels take on the appearance of a chessboard. The ceramic material from which the filter can be made has a pore size sufficient to allow gas permeability so that the pressure drop across the filter is relatively low, but which prevents the passage of soot. Thus soot is filtered from the exhaust gases.

EP-A-0341832 and corresponding case U.S. Pat. No. 4,902,487 describe a process and treatment system for soot-containing exhaust gas, the gas also containing nitric oxide (NO), which process comprising passing the gas unfiltered over an oxidation catalyst to convert NO to nitrogen dioxide (NO<sub>2</sub>), collecting the soot on a downstream filter and combusting the collected soot continuously at under 400° C. by reaction with the NO<sub>2</sub>, and there have been recent proposals to add further steps to that process and system for example nitrogen oxide (NOx) removal steps (see EP-A-0758713, EP-A-0341832 and U.S. Pat. No. 4,902,487 describing Johnson Matthey's Continuously Regenerating Trap (CRT™) technology and are incorporated herein by reference).

In the process described in EP-A-0341832 the oxidation step and the filter combustion step are carried out in two different honeycombs each in a separate shell or can or mounted within a single can. However, there are problems in adopting either embodiment. A problem with the former embodiment is that there can be limited space under-floor on a vehicle to mount each can. In the latter embodiment, a problem is that the construction of the can is complicated. If further downstream process steps are required these problems are exacerbated.

We have now found that these and other problems can be overcome or reduced by carrying out each of the treatment steps on a single wall-flow filter or single "brick". U.S. Pat. No. 5,089,237 discloses a soot burn-off filter for an exhaust system of a combustion engine, which filter includes a porous ceramic honeycomb block having channels plugged alternately at the ends to define a flow path through the partition walls of the channels, the walls at the inlet end having a catalytic coating. We understand from this document that the filter is used in a discontinuous process in which soot is allowed to accumulate on the filter and is periodically burnt off by raising the temperature and ensuring that sufficient oxygen (O<sub>2</sub>) is available. Owing to the combustion of a substantial quantity of soot in a relatively small space, temperatures high enough to produce destructive effects on the filter are readily attained. To limit such effect the filter of U.S. Pat. No. 5,089,237 provides a gas-tight region in the partition walls at the downstream end of the upstream channels. Although the catalytic coating is stated to lower the temperature at which soot combustion takes place, it evidently does not make the gas-tight region unnecessary.

According to one aspect, the invention provides a wall-flow filter for an exhaust system of a combustion engine, which filter comprises: a plurality of channels in honeycomb arrangement, wherein at least some of the channels are plugged at an upstream end and at least some of the channels not plugged at the upstream end are plugged at a downstream end; an oxidation catalyst on a substantially gas impermeable zone at an upstream end of the channels plugged at the downstream end; and a gas permeable filter zone downstream of the oxidation catalyst for trapping soot, characterised in that in an exhaust system the oxidation catalyst is capable of generating sufficient NO<sub>x</sub> from NO to combust the trapped soot continuously at a temperature less than 400° C.

The term "continuously" means that collected soot is combusted in a continuous exhaust gas flow; it thus excludes (except in the event of malfunction) the combustion of a large amount of accumulated soot. It does, however, encompass relatively minor variations in the level of collected soot and in the gas composition in response to normal variations of engine operating conditions and to short-term injection of reductant or NOx specific reactants in order to remove NOx downstream of the filter.

For the avoidance of doubt, by "absorb" herein, we mean to hold a relevant species on a relevant surface of a body (otherwise "adsorb") and/or to hold a species below the surface of a body i.e. within the body.

Exhaust gases from a combustion engine also contain unburnt hydrocarbon (HC), carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), steam (H<sub>2</sub>O(g)) and nitrogen (N<sub>2</sub>). Its content of NOx comprises NO and NO<sub>2</sub>, the majority being NO. At least sufficient NOx should be present to provide, after the catalytic oxidation of NO to NO<sub>2</sub>, at least enough NO<sub>2</sub> to oxidise the collected soot as it is formed, or after a small accumulation of soot. As described in the above mentioned EP-A-0341832, and in PCT application no. GB00/02062, additional NOx may be supplied by e.g. injecting nitric acid or the product of local oxidation of ammonia (NH<sub>3</sub>) or an ammonia precursor, such as urea.

The filter of the present invention provides a gaseous flow path defined in part by the open ends of each channel plugged at the downstream end, and the pores of the gas permeable wall of the channel. Soot in the gaseous exhaust enters the channel, but cannot pass through the pores of the channel wall. Thus soot is filtered from the gaseous exhaust by the pores of the filter. Furthermore, the gaseous exhaust is forced to flow over the entire zone supporting the oxidation catalyst, as the wall of the filter on which it is supported is substantially gas impermeable. This achieves the best possible yield of NO<sub>x</sub> from NO at a given temperature and also avoids caking the catalyst in soot.

Preferably, the arrangement of channels plugged at the upstream and downstream ends of the filter is such that each channel of the filter is plugged at one or other end thereof, and at the opposite end to the laterally and vertically adjacent channels, although other configurations can be used. For example, in an arrangement of striated appearance, a first longitudinal array of channels is plugged at one end, and the longitudinal arrays of channels either side of the first array are plugged at the opposite ends of the filter, and so on. The provision of a filter including at least some unplugged channels, thereby to act as a by-pass to the filter channels, is also within the ambit of the present invention. The unplugged channels can also be used to introduce a reactant required downstream of the wall-flow filter zone.

The channels are preferably square in cross-section but can be any other shape such as circular, rectangular, hexagonal or triangular.

Preferably, the oxidation catalyst, which is advantageously a compound including a platinum group metal (PGM), such as platinum (Pt) or palladium (Pd), blocks the filter pores in the gas impermeable zone, thereby making the zone substantially gas impermeable. Filter-grade materials for making the filter suitably have a mean pore diameter in the range 0.4 to  $20 \times 10^{-3}$  inch (1 to 50  $\mu\text{m}$ ) for gas treatments at about atmospheric pressure, but other values may be more appropriate for liquids or at higher or lower pressures. Although it is possible to manufacture a filter in which the filter material itself is gas impermeable or the pore size is graded so that the upstream part of channels plugged at the downstream end are gas impermeable but gas permeability increases towards the filter zone, we prefer that the filter material is of uniform pore size and that zones supporting the catalyst are rendered gas-impermeable by applying materials to them. When the filter is ceramic, it may be the product of shaping (e.g. by extrusion) and a composition containing sufficient fugitive material to leave, once removed e.g. by calcination, the required pores. The filter, whether ceramic or metal, may be the product of moulding and sintering a powder, possibly via foam. Whilst the filter material can be metal, we prefer it to be made of a ceramic material such as cordierite, alumina, mullite, silicon carbide, zirconia or sodium/zirconia/phosphate. The honeycomb has typically at least 50 cells per square inch (cpsi) ( $7.75 \text{ cm}^{-2}$ ), possibly more, e.g. up to 800 cpsi ( $124 \text{ cm}^{-2}$ ). Generally the range 100–600 cpsi ( $15.5\text{--}93 \text{ cm}^{-2}$ ) is preferred, of which 200–400 cpsi ( $31\text{--}62 \text{ cm}^{-2}$ ) is most preferred.

According to preferred embodiments, the downstream channels of the filter include a catalyst for a NOx absorber (NOx trap) and optionally a NOx reduction catalyst or Selective Catalytic Reduction (SCR) catalyst downstream of the NOx catalyst or Selective Catalytic Reduction (SCR) catalyst downstream of the NOx absorber. The combination of CRT™ technology and the SCR of NOx with a nitrogen-containing compound, such as NH<sub>3</sub> or urea, is described in our WO 99/39809. In a further embodiment, the channels upstream of the oxidation catalyst can include a sulphur oxides (SO<sub>x</sub>) absorber (SO<sub>x</sub> trap). The upstream SO<sub>x</sub> absorber can be included in embodiments with or without the NOx absorber or NOx reduction catalyst or SCR catalyst. As with the zone including the oxidation catalyst, in embodiments including one or more of the SO<sub>x</sub> absorber, NOx absorber or NOx reduction catalyst or SCR catalyst, the zones of each catalyst or absorber is substantially gas impermeable, and the gas impermeability is preferably provided by the catalyst or absorber or the catalyst or absorber support.

The NOx absorber/trap comprises a compound including an alkali metal, an alkaline earth, rare earth metal or transition metal or a mixed oxide capable of forming nitrates and/or nitrites of adequate stability in non-reducing conditions and of evolving nitrogen oxides and/or nitrogen in reducing conditions, an oxidation catalyst, preferably Pt, and a reduction catalyst, preferably rhodium (Rh). Composite oxides of e.g. alkaline earth metal and copper can also be used, such as (adopting periodic table letter codes) Ba—Cu—O or Mn<sub>2</sub>O<sub>3</sub>—BaCuO<sub>3</sub>, possibly with added CeO<sub>2</sub>, or Y—Ba—Cu—O and Y—Sr—Co—O. The NOx reduction catalyst will generally include one or more PGM, but especially Pt, Pt/Rh, Pd/Rh or Pt/Pd/Rh. The SCR catalyst can be a copper-based material, Pt, a mixed oxide of vanadia (V<sub>2</sub>O<sub>5</sub>) and titania (TiO<sub>2</sub>) or a zeolite or mixtures of two or more thereof and is preferably V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>/TiO<sub>2</sub>. Reference can be made to our WO 99/55446 and WO 99/39809 for further information. The SO<sub>x</sub> absorber can

include an alkaline earth metal oxide or alkali metal oxide or mixtures of any two or more thereof. Reference can be made to our EP-A-0814242 for further details.

In an exhaust system including an embodiment of the present invention including a NOx reduction catalyst or an SCR catalyst, the system can include means to inject reductant and/or NOx-specific reactant continuously or intermittently upstream of these catalysts. The oxidation catalyst of the invention can be in two parts, optimised respectively for oxidation of HC and CO and for conversion of NO to NO<sub>2</sub>. In the embodiment including both the NO<sub>x</sub> absorber and reduction catalyst, they can be in distinct regions of the filter or associated, for example co-precipitated or co-impregnated or present as sandwiched layers or as relatively fine (e.g. 1–500  $\mu\text{m}$ ) particles or overlaid in different washcoats.

Preferably, the or each catalyst or absorber is supported on a high-surface oxide support, preferably alumina (Al<sub>2</sub>O<sub>3</sub>), TiO<sub>2</sub> or zirconia (ZrO<sub>2</sub>), but the or each catalyst or absorber can be supported directly by the filter i.e. without additional high-surface oxide support.

Desirably, the catalyst(s) and, where present, absorber(s), whether supported on a high surface area oxide or directly by the filter, increases the local pressure-drop of the wall-flow filter by a factor of at least 2, and preferably up to 10. In one embodiment, the filter zone itself can be catalysed. A suitable catalyst is an oxidation catalyst to assist in combusting the soot, but more preferably the catalyst includes a base metal such as magnesium oxide (MgO) and most preferably the catalyst is a combination of lanthanum (La), calcium (Ca) and vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>). Where the base metal is MgO, a preferred catalyst is Pt on MgO. If the surfaces of the pores of the filter zone are to carry a catalyst, the pore diameter may be in the upper fifth of the above mentioned range or even higher, but such coating should be thin enough to avoid the need for large pores that would weaken the filter structurally.

"Alkali metal" as defined herein includes potassium (K), sodium (Na), lithium (Li), rubidium (Rb) or Cs; "alkaline earth metal" includes barium (Ba), calcium (Ca), strontium (Sr) or magnesium (Mg); and "rare earth metal" includes cerium (Ce), La or yttrium (Y) or other lanthanides.

The filter according to the invention can be packaged in any convenient way. Packaging materials commonly used in the art include a ceramic or steel wire mesh for wrapping and insulating the filter core, end plugs to prevent exhaust gas leaks through the wire mesh or to protect the mat; and steel for the shell or can. A suitable header can be used to provide the transition between the inlet and outlet pipes and the filter cross-section. Ports for the injection of additives or the introduction of sensor devices for on-board diagnostics can also be provided, where necessary.

The filter of the present invention can be made by methods known in the art, as exemplified by way of illustration only herebelow. In this aspect, the invention provides a method of making a filter according to the invention by stage-wise dipping in solutions and/or dispersions of precursors of the catalyst or absorber. In preferred features of this method, the method includes the steps of coating a wall of a channel of a wall-flow monolith with at least one material effective to decrease locally the gas permeability of the wall; and then applying to the coated wall at least one catalyst or absorber and optionally calcining the coated monolith.

However, we prefer to use the apparatus and method described in our WO 99/47260. To this end according to a further aspect, the invention provides a method of making a

filter according to the invention comprising, in either order, the steps of: (i) locating a containment means on top of a wall-flow monolith having a plurality of channels in honeycomb arrangement, wherein at least some of the channels are plugged at an upstream end and at least some of the channels not plugged at the upstream end are plugged at a downstream end; and (ii) dosing a pre-determined quantity of a liquid being a washcoat slurry or a solution of a catalyst or catalyst precursor, or a mixture of the two, into the containment means; and then (iii) by applying pressure or a vacuum, drawing said liquid component into at least a portion of the open wall-flow monolith channels, and retaining substantially all of the quantity within the channels.

In an alternative embodiment, the above method is applied to an unplugged monolith and the channels are plugged after the coatings have been applied. If one end of a channel is to be plugged, the method includes the step of removing coating applied to that end prior to plugging. Alternatively, the method includes the step of coating only the ends of channels which are predetermined to remain unplugged, i.e. the coating is not applied to an end of a channel which is to be plugged.

In a preferred feature, the method according to the invention comprises the step of applying a resist to a region where application of a washcoat or a solution or suspension of a catalyst or catalyst precursor or mixture thereof is to be delayed. The resist can be a wax or stearic acid, for example. exhaust system having a filter according to the invention. Preferably, the combustion engine is a diesel engine.

In another aspect, the invention provides a vehicle fitted with a combustion engine, preferably a diesel engine, including an exhaust system having a filter according to the invention.

According to a further aspect of the invention there is provided the use of a filter according to the invention for treating exhaust gases from a combustion engine, preferably a diesel engine.

In a further aspect, the invention provides a process for removing by combustion soot deposited on a filter disposed in an exhaust system of a combustion engine wherein exhaust gas containing NO is initially passed without filtering over an oxidation catalyst to convert NO in the exhaust gas to NO<sub>2</sub> prior to filtering to remove soot and wherein the exhaust gas containing NO<sub>2</sub> is then used to combust the soot trapped on the filter, the amount of NO converted to NO<sub>2</sub> being sufficient to enable combustion of soot trapped on the filter to proceed at a temperature less than 400° C., characterised in that the filter is a wall-flow filter, which filter comprises: a plurality of channels in honeycomb arrangement, wherein at least some of the channels are plugged at an upstream end and at least some of the channels not plugged at the upstream end are plugged at a downstream end; the oxidation catalyst is on a substantially gas impermeable zone at an upstream end of the channels plugged at the downstream end; and a gas permeable filter zone downstream of the oxidation catalyst for trapping soot.

In order that the invention may be more fully understood, reference will be made to the accompanying drawing which shows an elevated cross-sectional view of one embodiment of a filter according to the present invention.

#### BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 shows three adjacent channels 4, 6, 8 of a cordierite honeycomb filter 10, having 200 cpsi (31 cm<sup>-2</sup>) and, before use, pores of approximately 10 µm in diameter. Channel 6 is plugged at 12 at the upstream end of the filter 10 and the other two channels 4, 8 are each plugged at 14 at the

downstream end of the filter 10. Thus, gas entering two channels 4, 8 are each plugged at 14 at the downstream end of the filter 10. Thus, gas entering channel 6 at the upstream end must pass through the walls of the channel 6 to reach the downstream end of the filter 10. Over a region or zone extending downstream of the opening to channel 6, the walls carry coating 16 comprising an Al<sub>2</sub>O<sub>3</sub> washcoat support and a metallic Pt oxidation catalyst. Coating 16 obstructs the pores of the filter walls. Over a region or zone extending upstream from the outlet to filter 10, channels 4 and 8 carry coatings 18, 20 comprising a NOx absorber composition including barium oxide (BaO) and a NOx reduction catalyst composition comprising Pt/Rh. In order to make the coatings 18, 20, the zone to be coated with coating 20 is first covered with a resist, such as wax or stearic acid, during application of coating 18. In this embodiment the regions of the cordierite filter 10 including coatings 16 and 18 are rendered gas impermeable by the presence of the coating. Between coatings 16 and 18, the walls of the channels 4, 6, 20 8 remain gas permeable and provide a filter zone 22.

Diesel exhaust gas entering the reactor undergoes oxidation of HC, CO and NO in presence of coating 16. Soot in the gas is collected on the walls of channels 4, 6, 8 at filter zone 22 and is combusted by NO<sub>x</sub> derived from the oxidation of NO. The gas, containing soot combustion products, passes through the wall of the filter and contacts the NOX trap coating 18, which absorbs NO. When sufficient NO<sub>2</sub> is stored (as the nitrate, for example), which can be ascertained by the on-board diagnostics of the vehicle, coating 18 can be regenerated with a rich pulse of gaseous exhaust i.e. gas including excess reductant such as HC. The rich/lean cycling can be controlled using the vehicle's engine management system. The resulting NOX-rich gas contacts coating 20 including the NOX reduction catalyst, which effects oxidation of HC and CO and reduction of NO<sub>x</sub> to N<sub>2</sub>. Alternatively, where coating 20 is a SCR catalyst, NO-specific reactant such as ammonia can be injected at an upstream end of the filter at a rate and temperature permitting unreacted ammonia to slip oxidation catalyst 16 and contact absorber 18, which it regenerates, and catalyst 20, over which it reduces NO<sub>x</sub> to N<sub>2</sub>.

In order that one method of manufacture of the filter according to the invention may be more fully understood, the following Example is provided by way of illustration 45 only.

The substrate is a filter grade cordierite honeycomb monolith of square cross-section channels 30 mm in diameter and 150 mm long and having a mean pore diameter 10 µm in which half of the passages both ends of the monolith are plugged so that each channel of the monolith is plugged at one or other end thereof, and at the opposite end to the laterally and vertically adjacent channels.

One end of the monolith is labelled 'inlet' and is dipped 55 25 mm deep into an aqueous dispersion of hydrated Al<sub>2</sub>O<sub>3</sub>, then withdrawn, dried at 100° C. and allowed to cool. The inlet end is then dipped to the same depth in an aqueous solution of 2% w/w platinum chloride. The monolith is dried as before.

The unlabelled end of the monolith is prepared by firstly dipping it to a depth of 25 mm in turn in an aqueous solution of sodium stearate and then drying the resulting monolith at 100° C. The resulting monolith is then dipped in aqueous hydrochloric acid and then water (two changes), to rinse off solubles. This procedure produces an insoluble stearic acid layer as a resist, which excludes any materials applied in neutral or acidic solution. The resist-coated monolith is then

dipped to a depth of 50 mm, into an aqueous solution of barium acetate and platinum chloride, and then dried. This dip applies these materials to an area upstream of the resist-coated area. Then the coated monolith is dipped in 5% w/w aqueous sodium hydroxide to a depth of 25 mm to dissolve the stearic acid resist. This step is repeated twice and is followed by two rinses with water. The coated monolith is then dried. The resulting monolith is then dipped to a depth of 25 mm in the  $\text{Al}_2\text{O}_3$  dispersion used at the inlet end, and described above. The coated monolith is then dried. Finally, to a depth of 25 mm in Pt/Rh solution. The coated monolith is then dried.

The resulting monolith is then calcined at 500° C. for 1 hr to convert the metal salts to oxides or metals and to develop the surface area of the  $\text{Al}_2\text{O}_3$  to provide a filter according to the invention.

What is claimed is:

1. A wall-flow filter for an exhaust system of a combustion engine, which filter comprises: a honeycomb arrangement defining a plurality of first channels plugged at an upstream end and a plurality of second channels not plugged at the upstream end but plugged at a downstream end; an oxidation catalyst on a substantially gas impermeable zone at an upstream end of the second channels; and a catalyst-free gas permeable filter zone downstream of the oxidation catalyst for trapping soot, wherein the oxidation catalyst is capable of generating sufficient  $\text{NO}_2$  from  $\text{NO}$  to combust the trapped soot continuously at a temperature less than 400° C.

2. A filter according to claim 1, wherein the arrangement of the first and second channels is such that laterally and vertically adjacent channels are plugged at opposite ends.

3. A filter according to claim 1, wherein the honeycomb arrangement further comprises a plurality of third channels which are unplugged to provide a flow-through-by-pass to the first and second channels.

4. A filter according to any of claim 1, wherein the oxidation catalyst includes a platinum group metal.

5. A filter according to claim 4, wherein the platinum group metal comprises at least one of Pt and Pd.

6. A filter according to claim 1, further comprising a NO<sub>x</sub> absorber on a substantially gas impermeable zone on the first channels.

7. A filter according to claim 6, wherein the NO<sub>x</sub> absorber includes an alkali metal, an alkaline earth metal or rareearth metal or mixtures of any two or more thereof.

8. A filter according to claim 6, wherein the NO<sub>x</sub> absorber includes an oxide of at least one of an alkali metal and an alkaline earth metal.

9. A filter according to claim 6, further comprising a NO<sub>x</sub> reduction catalyst or a Selective Catalytic Reduction (SCR)

catalyst on a substantially gas impermeable zone on the first channels downstream of the NO<sub>x</sub> absorber.

10. A filter according to claim 9, wherein the SCR catalyst includes copper-based materials, Pt, a mixed oxide of vanadium and titanium or a zeolite or mixtures of two or more thereof.

11. A filter according to claim 9, wherein the NO<sub>x</sub> reduction catalyst comprises at least one platinum group metal.

12. A filter according to claim 11, wherein the platinum group metal is selected from the group consisting of Pt, Pt/Rh, Pd/Rh or Pt/Pd/Rh.

13. A filter according to claim 9, wherein the SCR catalyst comprises  $\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$ .

14. A filter according to claim 6, wherein the alkali metal is potassium, sodium, lithium, rubidium or caesium or a mixture of any two or more thereof, the alkaline earth metal is barium, calcium, strontium or magnesium or a mixture of any two or more thereof or the rare earth metal is cerium, lanthanum or yttrium or other lanthanide or a mixture of any two or more thereof.

15. A filter according to claim 1, further comprising a SO<sub>x</sub> absorber on a substantially gas impermeable zone on the second channels upstream of the oxidation catalyst.

16. A filter according to claim 15, wherein the SO<sub>x</sub> absorber includes an alkaline earth metal oxide or alkali metal oxide or mixtures of any two or more thereof.

17. A filter according to claim 16, wherein the alkali metal is potassium, sodium, lithium, rubidium or caesium or a mixture of any two or more thereof, and the alkaline earth metal is barium, calcium, strontium or magnesium or a mixture of any two or more thereof.

18. A filter according to claim 1, further comprising a high-surface oxide support comprising alumina, titania or zirconia for supporting the catalyst.

19. A filter according to claim 1, wherein the support supporting the catalyst renders the zone including the catalyst substantially gas impermeable.

20. A filter according to claim 1, wherein the presence of the catalyst increases the local pressure drop of the wall-flow filter by a factor of at least 2.

21. A combustion engine including an exhaust system having a filter according to claim 1.

22. A diesel engine according to claim 21.

23. A vehicle fitted with a combustion engine according to claim 21.

24. A filter according to claim 1, wherein the presence of the catalyst increases the local pressure drop of the wall-flow filter by a factor of at least 10.

\* \* \* \* \*

UNITED STATES PATENT AND TRADEMARK OFFICE  
CERTIFICATE OF CORRECTION

PATENT NO. : 6,753,294 B1  
DATED : August 2, 2004  
INVENTOR(S) : Robert James Brisley et al.

Page 1 of 1

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Title page.

Item [56], References Cited, FOREIGN PATENT DOCUMENTS, delete  
"EP 0 736 713 2/1997" and insert therefor -- EP 0 736 503 10/1996 --;  
insert -- EP 0 758 713 2/1997 --.

Column 7.

Line 36, after "according to," delete "any of."  
Line 44, delete "rerearth" and insert therefor -- rare earth --.

Signed and Sealed this  
Twelfth Day of October, 2004



JON W. DUDAS  
*Director of the United States Patent and Trademark Office*

## Beyond Traditional Ceramic Honeycombs

by Bilal Zuberi Ph.D.  
Art O'Dea

Posted: January 1, 2008

Cellular honeycomb ceramics have been used in a variety of applications, including support materials for catalytic conversion, adsorptive separations, membrane supports, cross-flow filtration and fluid filtration. The honeycomb design offers a remarkably high geometric surface area per unit volume and improves the chemical residence times for reactions to reach completion in high-flow conditions. Extrusion is a well-understood and highly scalable ceramic forming process, and extruded cellular honeycomb monoliths provide unmatched structural rigidity and robustness.

### Existing Systems Face Limitations

One of the best-known uses of honeycomb materials is in gasoline automobile catalytic converters. Since the late 1970s, every car on the road in the U.S. has been equipped with a honeycomb catalytic converter under the chassis. These converters provide a complex chemical reactor to reduce emissions of regulated gas species from gasoline engines. Ceramic flow-through honeycombs have been used in converters because of their high mechanical and chemical durability (see Figure 1). Typically, these ceramic honeycombs are made by extruding powder-based materials like alumina, mullite and silicon carbide. The most common material used in these applications is cordierite, which features a low coefficient of thermal expansion (CTE).

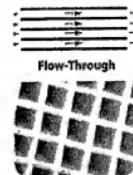
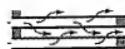


Figure 1. In the flow-through configuration, cross-flow through the walls is extremely limited.

The cellular geometry of the honeycomb provides a high surface area per unit volume for deposition of catalysts or absorptive materials. For example, in the case of a gasoline-powered car, a layer of high-surface-area alumina washcoat is placed on the wall, and precious metal catalysts are dispersed finely on the washcoat bed. At high temperatures, the reactions occur quickly but are typically mass-flow limited in a laminar-flow regime. In the flow-through configuration, cross-flow through the walls is extremely limited.



Wall-Flow

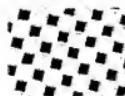


Figure 2. Alternate channels are

While the flow-through configuration of honeycomb ceramics works well for laminar-flow catalytic conversion, its utility is limited in filtration. Unlike gasoline engines, diesel engines emit gas- and condensed-phase toxic emissions. When these engines became popular for use in the European light-duty market, the emission control industry recognized a need for soot nano-particle filtration functionality. As a result, the wall-flow design was added to increase filtration functionality while retaining the benefits of the cellular honeycomb structure (see Figure 2).

*blocked in the wall-flow design, leading to turbulent flow and forced convection of fluid through the permeable walls of the honeycomb.*

Alternate channels are blocked in the wall-flow design, leading to turbulent flow and forced convection of fluid through the permeable walls of the honeycomb. As the fluid is forced through the wall, filtration of suspended particulate matter takes place while fluid passes through unobstructed. Depending on the size of the particles, diffusion, inertial and interception mechanisms lead to the entrapment of suspended particles on the wall.

In order to create a gas-permeable wall microstructure out of the standard flow-through honeycomb material, the internal wall porosity of powder-based chemistries was increased. Since then, however, the microstructure has been deemed ill-suited for such applications. Unfortunately, the obstruction to flow is relatively high in powder-based honeycomb filters, which leads to backpressure and poor filtration efficiency.

Studies of this obstruction of flow affirm that powder-based media, however porous, are not ideal for the filtration of particles in the nanometer and micrometer size ranges. Advanced filters in applications as diverse as high-efficiency particulate air (HEPA) filtration and air-oil separation have typically relied on fiber-based filtration media. The cross-linked microstructure formed by intersecting and overlapping fibers improves filtration performance without causing significant backpressure. However, until now, this desired microstructure was not available in a robust and durable extruded honeycomb form. Pleated and rolled fiber-paper sheets do not allow for robust filters, and they often exhibit a telescoping failure mode, among other problems.

## Developing a New Alternative

New extruded ceramic honeycombs\* have been developed with a unique cross-linked pore microstructure in multiple chemistries. The resulting honeycombs have a high cell density, which leads to high geometric surface area. In addition, high permeability of the wall microstructure results in low filtration backpressure, and the interconnected pore architecture enables high filtration efficiency.

Depending on the fabrication parameters, filters can capitalize on diffusion flow to achieve extremely high nano-particle filtration efficiencies. In addition, benefits such as structural rigidity, robustness and low cost of production are also achieved. By altering the fiber and bonding composition chemistry and processing conditions, high-porosity cellular honeycombs with mullite, silicon carbide, cordierite, alumina and steel alloys have been developed.



Figure 3. A top view of two parallel channels in an extruded porous honeycomb with the patented cross-linked microstructure.

Figure 3 shows a top view of two parallel channels in an extruded porous honeycomb with the patented cross-linked microstructure. The filtration media in the cellular honeycomb closely resembles the kind of surface texture and structure expected in the typical fiber-based membranes or candle-type tube and bag filters—but in an extruded, monolithic honeycomb geometry. The requirements and processing conditions for mixing, extruding, drying and firing the materials into numerous desired honeycomb configurations have been

determined. Furthermore, based on application needs, similar internal cross-linked wall microstructures can be created in several chemistries by altering material and processing parameters.

\*Developed and patented by GEO<sub>2</sub> Technologies.

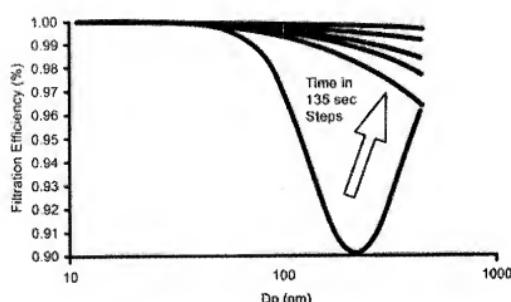


Figure 4. The size-specific filtration efficiency of a wall-flow filter located downstream of a soot generator source.

Figure 4 shows the size-specific filtration efficiency of a wall-flow filter measured using a scanning mobility particle sizer (SMPS, 135-second scans across the diameter range) downstream of a soot generator source. The filter had an average pore size of 15 µm with a narrow distribution curve. As can be seen, not only is the initial particle filtration efficiency very high, but the filtration efficiency also continues to improve as a fine layer of soot cake builds up on the filter.

The internal pore microstructure of the honeycombs provides additional "open" and "available" porosity for the placement of reactive or catalytic species in the pore volume. For example, in the case of wall-flow honeycombs for use in turbulent flow fixed-bed chemical conversion reactors, the catalytic material can be dispersed throughout the internal porosity of the walls (see Figure 5). This is achieved without causing significant obstruction to the flow of fluids through the wall.

This scenario has been tested in the case of automotive emissions control, where low backpressures were measured on a filter and compared to a standard particle-based cordierite filter. Despite having five times the typical washcoat loading, the filter exhibited lower backpressure and higher catalyst efficiency than the standard filters.

In the case of a wall-flow configuration, fluids such as gases from engine exhaust are forced through the wall structure where they come into direct contact with the residing catalyst. Instead of the gas-phase reactions being rate-limited by mass transfer in the channels, as is the case in flow-through honeycombs, the reactions become pore-diffusion limited, which is much more effective. The induced turbulence leads to an overall increase

The patented, cross-linked microstructure of the new honeycomb substrates and processes provide several advantages over conventional powder-based ceramics. The fiber-based structure exhibits a mechanical strength similar to low-porosity, powder-based filters (~ 45% porous), but at a porosity of greater than 65%. Depending on the pore size distribution, > 99% filtration efficiencies for nano-particles (10-470 nm) have been observed.

For example, Figure 5 shows the size-



Figure 5. In wall-flow honeycombs for use in turbulent flow fixed-bed chemical conversion reactors, the catalytic material can be dispersed throughout the internal porosity of the walls.

in reaction rates and better utilization of catalyst loadings.



*Figure 6. Honeycomb structures with a highly permeable, cross-linked pore microstructure can be used as membrane support structures for adsorptive reaction, catalytic conversion or cross-flow filtration-type applications.*

Finally, honeycomb structures with a highly permeable, cross-linked pore microstructure can also be used as membrane support structures for adsorptive reaction, catalytic conversion or cross-flow filtration-type applications (see Figure 6). Membranes, including zeolite-based or polymeric types, placed as a layer on top of the honeycomb structures can act as the active layers while the honeycomb provides a robust and permeable structure for high-flow-rate and otherwise harsh operating conditions.

### **Additional Applications on the Horizon**

The new honeycomb structures in wall-flow and flow-through configurations are already in use for several applications, including diesel particulate filters, air-oil separators, selective absorption of contaminants in gases and multi-functional catalytic conversion.

Additional applications are planned in a wide variety of areas, including gas separations, alcohol-water separations, water filtration and bio-filtration.

*For more information regarding cellular honeycomb ceramics, contact GEO<sub>2</sub> Technologies Inc., 12-R Cabot Rd., Woburn, MA 01801; (781) 569-0559; fax (781) 721-6301; e-mail [info@geo2tech.com](mailto:info@geo2tech.com); or visit [www.geo2tech.com](http://www.geo2tech.com).*

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